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New Catalytic System for Activation of Alkane and Arene C-H Bonds on the Basis of Platinum(II) Complexes and Tetrachloromethane

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Abstract

Alkanes and alkylarencs RH (cyclohexane, n-hexane, toluene) in a mixture with CCl4 and MeCN (1:1:1, by volume), at temperatures of 110°C and higher, in the presence of platinum complexes of the formula cis-PtX2(L)2 (X = Cl, Ph, L = PPh3; X = Cl, L = MeCN), react to form chloroform and chloride RCl. Catalytic activity decreases in the order PtPh2(PPh3)2 (3.9) > PtCl2(PPh3)2 (1.0) > PtCl2(MeCN)2 (0.24). In the case of n-hexane, C-H bonds at the secondary carbon atoms are by a factor of 11 more active than those at the primary atom, and in the case of toluene, benzyl chloride is the main reaction product (99%). The reaction is first-order in cyclohexane, metal complex, and tetrachloromethane. The chlorination of toluene is zero-order in hydrocarbon. The results of kinetic studies permit to conclude that the role of the catalyst is to activate the tetrachloromethane C-Cl bonds by an oxidative addition scheme.